

JUL 13 2015

PTC5170 04-05

Approved for use through 07/31/2006. OMB 0851-0001
U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE
is a collection of information unless it contains a valid OMB control number.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

| | | |
|--|------------------------------|------------------|
| Request for Continued Examination (RCE) Transmittal Address to: Mail Stop RCE Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450 | Application Number | 10727709 |
| | Filing Date | 12/04/2003 |
| | First Named Inventor | Zhenan Bao |
| | Art Unit | 2814 |
| | Examiner Name | Douglas A. Wills |
| | Attorney/Agent Number | BAO 39 |

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application. Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1990, or to any design application. See Instruction Sheet for RCEs that is submitted to the USPTO on page 2.

1. **Submission required under 37 CFR 1.114** Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____

ii. ☐ Other _____

b. ☒ Enclosed

i. ☐ Amendment/Reply

ii. ☐ Affidavit(s)/ Declaration(s)

iii. ☒ Information Disclosure Statement (IDS)

iv. ☐ Other _____

2. **Miscellaneous**

a. ☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of _____ months. (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(f) required)

b. ☐ Other _____

3. **Fees**

The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.

The Director is hereby authorized to charge the following fees, any underpayment of fees, or credit any overpayments, to Deposit Account No. 00-2355. I have enclosed a duplicate copy of this sheet.

a. ☒

i. ☒ RCE fee required under 37 CFR 1.17(e)

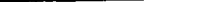
ii. ☐ Extension of time fee (37 CFR 1.138 and 1.17)

iii. ☐ Other _____

b. ☐ Check in the amount of \$ _____ enclosed

c. ☐ Payment by credit card (Form PTO-2038 enclosed)

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2033.

| | | | |
|---|---|------------------|---------|
| SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED | | | |
| Signature |  | Date | 6/29/05 |
| Name (Print/Type) | Ronald J. Corbett | Registration No. | 47,500 |

| CERTIFICATE OF MAILING OR TRANSMISSION | | |
|--|--|-------------------------------|
| <p>I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Mail Stop RICE, Communications for Patents, P. O. Box 1450, Alexandria, VA 22313-1450 or facsimile transmitted to the U.S. Patent and Trademark Office on the date shown below.</p> | | |
| <p>Signature</p> <p><i>Mark R. Rice</i></p> | <p>Name (Print Type)</p> <p>Mark R. Rice</p> | <p>Date</p> <p>08/30/2005</p> |

This collection of information is required by 37 CFR 1.144. The information is required to create or retain a benefit by the public which is in the interest of the USPTO to process an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 15 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1480, Alexandria, VA 22312-1480. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop RICE, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PAGE 313 * RCVD AT 71132005 10:36:52 AM (Eastern Daylight Time) * SVR:USPTO-EFXRF-178 * DHS:2733309 * CSD:377 480 8866 * DURATION (mm:ss):05:30

22/2005 .WISE1 00000001 082395 10727709

FC:1801 790.00 DB

Adjustment Date: 09/29/2005 SDIRETA1
07722/2005 LWISE1 00000001 082395 10727709
01 FC:1801 790.00 CR

BEST AVAILABLE COPY

AUG. 3. 2005 5:56PM HITT GAINES 9724808865
ATTORNEY DOCKET NO.: BAU 39

NO. 1639 P. 2
PATENT

PATENT AND TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Zhenan Bao, et al.

2005 AUG - 3 PM 3:15

Serial No.: 10/727,709

RECEIVED
US PATENT & TRADEMARK OFFICE
CENTRAL FAX CENTER

Filed: December 4, 2003

AUG 03 2005

Title: ORGANIC FIELD EFFECT TRANSISTORS WITH ACTIVE CHANNELS
FORMED OF DENSIFIED LAYERS

Group Art Unit: 2814

Examiner: Waising Louie

Mail Stop 16
Director of the US Patent and
Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

I hereby certify that this correspondence is being facsimile transmitted to the
Patent and Trademark Office (Fax No. (571) 273-8300) on August 3, 2005

Marty Balko
Printed or typed name of person signing the certificate

8-3-05
Date of Mailing

Marty Balko
Signature of person mailing

Sir:

REQUEST FOR REFUND

On June 30, 2005 we filed an RCE and Foreign Search Information Disclosure Statement via facsimile to the USPTO in connection with the above-referenced case (see Attachment A). As you can see, on our Deposit Account Statement of July 2005 (see Attachment B), we were charged twice for the RCE fee: once on July 12, 2005 and the second time on July 22, 2005. We therefore request that the refund of the second RCE fee of \$790.00 which was withdrawn from the deposit account be refunded to our deposit account 082395.

Respectfully submitted,

HITT GAINES, P.C.

Ronald J. Corbett
Ronald J. Corbett
Reg. No. 47,500

Date: August 3, 2005
Hitt Gaines, P.C.
P.O. Box 832570
Richardson, Texas 75083-2570
(972) 480-8800

AUG. 3. 2005 5:56PM HITT GAINES 9724808865

NO. 1639 P. 3

P. 1

* * * COMMUNICATION RESULT REPORT (JUN. 30. 2005 9:06AM) * * *

FAX HEADER 1: HITT GAINES 9724808865
FAX HEADER 2:

TRANSMITTED/STORED : JUN. 30. 2005 9:00AM
FILE MODE OPTION

| 1229 MEMORY TX | ADDRESS | RESULT | PAGE |
|----------------|---------|--------|-------|
| G3 | USPTO | OK | 13/13 |

REASON FOR ERROR
E-1) HANG UP OR LINE FAIL
E-2) NO ANSWER
E-3) MAIL SIZE OVER

E-2) BUSY
E-3) NO FACSIMILE CONNECTION

HITT GAINES, P.C.
Intellectual Property Law & Related Matters

RECEIVED
CENTRAL FAX CENTER
AUG 03 2005

FACSIMILE TRANSMISSION

TO: USPTO
Examiner Douglas A. Wille; Art Unit 2814

FAX NO. (571) 273-1721 (direct fax number for Examiner Wille)

FROM: Ronald J. Corbett

RE: Serial No.: 10/727,709
Attorney Docket No.: BAO 39
LUCT-125888

DATE: June 30, 2005

PAGES: 13 (including cover page)

If you do not receive the indicated number of pages, please notify the sender at the telephone number shown below. Thank you.

THE INFORMATION CONTAINED IN THIS FACSIMILE TRANSMISSION IS AN ATTORNEY-CLIENT PRIVILEGED, CONFIDENTIAL COMMUNICATION INTENDED FOR THE EXCLUSIVE USE OF THE INTENDED RECIPIENT NAMED ABOVE. IF YOU ARE NOT THE INTENDED RECIPIENT, OR ARE AN EMPLOYEE OR AGENT RESPONSIBLE FOR DELIVERING THIS TRANSMISSION TO THE INTENDED RECIPIENT, YOU ARE HEREBY NOTIFIED THAT ANY DISSEMINATION, DISTRIBUTION OR COPYING OF THIS TRANSMISSION IS STRICTLY PROHIBITED. IF YOU HAVE RECEIVED THIS TRANSMISSION IN ERROR, PLEASE NOTIFY THE SENDER IMMEDIATELY AT THE TELEPHONE NUMBER SHOWN BELOW AND MAIL THE ORIGINAL TRANSMISSION TO THE ADDRESS BELOW. WE WILL REIMBURSE YOU FOR ANY REASONABLE EXPENSE YOU MAY INCUR DOING SO. THANK YOU.

MESSAGE:

Please send fax confirmation to: 972-480-8865

If attachment is not legible, please call me at 972-480-8800.
Thank you!

Marty Balko
(assistant to Ron Corbett)

Mailing Address: P.O. Box 832570, Richardson, Texas 75083-2570
Street Address: Palisades Central II, 2435 North Central Expressway, Suite 1300, Richardson, Texas 75080-2753 U.S.A.
Tel: (972) 480-8800 Fax: (972) 480-8865 rm@hittgaines.com

Attachment A

PAGE 3/17 * RCVD AT 8/3/2005 6:57:00 PM [Eastern Daylight Time] * SVR:USPTO-EFAXF-6/25 * DNIS:2738300 * CSID:972 480 8865 * DURATION (mm-ss):05:42

PTO/SB/97 (08-03)
Approved for use through 07/31/2006. OMB 0851-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Certificate of Transmission under 37 CFR 1.8

I hereby certify that this correspondence is being facsimile transmitted to the United States Patent and Trademark Office

on June 30, 2006
Date

- Request for Continued Examination (RCE) Transmittal (pp 1);
- Foreign Search IDS (pp 2) with cited reference; and
- IDS by Applicant (pp 2).


Signature

Marty Balko

Typed or printed name of person signing Certificate

Note: Each paper must have its own certificate of transmission, or this certificate must identify each submitted paper.

This collection of information is required by 37 CFR 1.8. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1.8 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

AUG. 3. 2005 5:57PM

HITT GAINES 9724808865

RECEIVED
CENTRAL FAX CENTER

NO. 1639 P. 5

AUG 03 2005

PTO/SB/30 (04-05)

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.
Approved for use through 07/31/2008, OMB 0831-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCERequest
for
Continued Examination (RCE)
TransmittalAddress to:
Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

| | |
|------------------------|------------------|
| Application Number | 10/727,709 |
| Filing Date | 12/04/2003 |
| First Named Inventor | Zhenan Bao |
| Art Unit | 2814 |
| Examiner Name | Douglas A. Wille |
| Attorney Docket Number | BAO 39 |

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application. Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. See Instruction Sheet for RCEs (not to be submitted to the USPTO) on page 2.

1. **Submission required under 37 CFR 1.114** Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____

ii. ☐ Other _____

b. ☒ Enclosed

i. ☐ Amendment/Reply

ii. ☐ Affidavit(s)/ Declaration(s)

iii. ☒ Information Disclosure Statement (IDS)

iv. ☐ Other _____

2. **Miscellaneous**

a. ☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of _____ months. (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

b. ☐ Other _____

3. **Fees**

The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.

a. ☒ The Director is hereby authorized to charge the following fees, any underpayment of fees, or credit any overpayments, to Deposit Account No. 08-2395. I have enclosed a duplicate copy of this sheet.

i. ☒ RCE fee required under 37 CFR 1.17(e)

ii. ☐ Extension of time fee (37 CFR 1.136 and 1.17)

iii. ☐ Other _____

b. ☐ Check in the amount of \$ _____ enclosed

c. ☐ Payment by credit card (Form PTO-2038 enclosed)

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

| | | | | |
|-------------------|--------------------------|------------------|---------|------------|
| Signature | <i>Ronald J. Corbett</i> | Date | 6/19/05 | 08/30/2005 |
| Name (Print/Type) | Ronald J. Corbett | Registration No. | 47,500 | |

CERTIFICATE OF MAILING OR TRANSMISSION

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Mail Stop RCE, Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450 or facsimile transmitted to the U.S. Patent and Trademark Office on the date shown below.

| | | | |
|-------------------|--------------------|------|------------|
| Signature | <i>Marty Balke</i> | Date | 06/30/2005 |
| Name (Print/Type) | Marty Balke | | |

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop RCE, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.
If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

AUG. 3. 2005 5:57PM

HITT GAINES 9724808865

NO. 1639 P. 6

RECEIVED
CENTRAL FAX CENTER

AUG 03 2005

DOCKET NO. BAO-39

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Zhenan Bao

Serial No.: 10/727,709

Filed: December 4, 2003

For: ORGANIC FIELD EFFECT TRANSISTORS WITH ACTIVE CHANNELS
FORMED OF DENSIFIED LAYERS

Group No.: 2811

Examiner: Douglas A. Wille

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

I hereby certify that this correspondence is being facsimile transmitted to the
Patent and Trademark Office (Fax No. (703) 572-9305) on June 28, 2005

Marta Ballo
Printed or typed name of person signing the certificate

6-30-05
Date of Mailing

Marta Ballo
Signature of person mailing

Sir:

FOREIGN SEARCH INFORMATION DISCLOSURE STATEMENT

In accordance with 37 C.F.R. §1.56 and the provisions of 37 C.F.R. §§1.97 and 1.98 and §609 of the Manual of Patent Examining Procedure, Applicant hereby makes a disclosure of the patents, publications and other information listed below and on the accompanying form IDS by Applicant, which may be potentially material to the patentability of the invention disclosed in the above-referenced application. Pursuant to § 1.97(e) the Applicant hereby states that each item of information contained in the information disclosure statement was cited in a communication from a

foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement.

U.S. Patent No.

Inventor

Date

5,546,889

Wakita, et al.

August 20, 1996

Other References:

YU-TAITAO, et a. "Structure Evolution of Aromatic-Derivatized Thiol Monolayers on Evaporated Gold", Langmuir, Volume 13, No. 15 (1997), pages 4018-4023.

As attorney for the Applicant, I am signing below on the basis of the information supplied by an individual designated in § 1.56(c).

The Commissioner is hereby authorized to charge any fees or credit any overpayments to Deposit Account No. 08-2395.

Respectfully submitted,

HITT GAINES, P.C.



Ronald J. Corbett
Registration No. 47,500

Date: June 30, 2005

Hitt Gaines, P.C.
P.O. Box 832570
Richardson, Texas 75083-2570
(972) 480-8800

PTO/SE/D&A (08-03)

Approved for use through 07/31/2006. OMB 0651-0031

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Substitute for form 1449/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet

1

2

2

Complete If Known

| | |
|--------------------|------------|
| Application Number | 10/727.709 |
|--------------------|------------|

| | |
|-------------|------------------|
| Filing Date | December 4, 2003 |
|-------------|------------------|

| | |
|----------------------|------------|
| First Named Inventor | Zhenan Bao |
|----------------------|------------|

| | |
|----------|------|
| Art Unit | 2811 |
|----------|------|

| | |
|---------------|------------------|
| Examiner Name | Douglas A. Wille |
|---------------|------------------|

| | |
|------------------------|--------|
| Attorney Docket Number | BAO-39 |
|------------------------|--------|

[illegible][illegible]

| | | | |
|--------------------|--|-----------------|--|
| Examiner Signature | | Date Considered | |
|--------------------|--|-----------------|--|

*EXAMINER: Initial if reference considered, whether or not citation is in compliance with 48 CFR 101-11.6.

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 806. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. ¹ Applicant's unique citation designation number (optional). ² See Kinda Codes of USPTO Patent Documents at www.uspto.gov or MPEP 801.04. ³ Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). ⁴ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁵ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁶ Applicant is to place a check mark here if English language translation is attached.

This collection of information is required by 37 CFR 1.57 and 1.88. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.

Structure Evolution of Aromatic-Derivatized Thiol Monolayers on Evaporated Gold

Yu-Tai Tao,* Chien-Ching Wu, Ji-Yang Eu, and Wen-Ling Lin

Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China

Kwang-Chen Wu and Chun-hsien Chen*

Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China

Received January 31, 1997; In Final Form May 12, 1997

The structure of self-assembled monolayers of thiophenols (I), benzyl mercaptans (II), biphenylthiols (III), and 4-biphenylmethanethiols (IV) on the surface of Au(111) are compared using cyclic voltammetry, reflection absorption infrared spectroscopy, scanning tunneling microscopy, ellipsometry and contact angle measurement. The results suggest that benzyl mercaptans and 4-biphenylmethanethiols form closely packed and ordered monolayer, irrespective of the length of a *p*-alkoxy substituent. For thiophenol and biphenylthiol, a film of lower surface coverage was formed. A long *p*-alkoxy chain (*n*-C₁₈H₃₇O) increases the intermolecular interaction and leads to a closer packing within the monolayer film. The difference is attributed to the interplay between intermolecular interaction and the bond angle preference at the thiolate head group.

Introduction

The self-assembling of organothiol on gold to form a monolayer has attracted much attention lately both from the fundamental point of view and from their application prospects.¹ In most applications, structural order and integrity of the film are of major concern. A simple alkanethiol monolayer is one of the most thoroughly studied self-assembled monolayer (SAM) systems. Detailed structural information regarding the packing, orientation, as well as conformation of the molecular chains have been accumulated by various analytical techniques.²⁻¹¹ The aromatic-containing monolayer is of importance because many optoelectronic applications involve an aromatic chromophore as the functioning unit. Many studies of aromatic-containing monolayers on gold have been reported, with the aromatic moiety as the only major component or as a part of a chain or in the presence of other functional groups.¹²⁻²⁷ It has been shown that such molecules anchor on gold substrates predominantly

through the sulfur atom instead of the aromatic ring.¹² Nevertheless, a variety of structural details are proposed. It is noted that for the simplest member of the arylthiol, thiophenol, the detailed structure has not been unambiguously determined. On the basis of several methods, Sabatani *et al.*¹² concluded that thiophenol forms poorly defined monolayers. Well-ordered lattice structure was not found by high-impedance scanning tunneling microscopy (STM) for thiophenol monolayer either.¹³ With an increase of the number of aromatic moieties, the monolayers become either more densely packed or well ordered,^{14,15} presumably a result of stronger adsorbate-adsorbate interactions. The effect of a pending alkyl chain on the packing is not well understood.^{16,17}

In this paper we wish to report our further structural studies for monolayers formed by a series of aromatic-derivatized thiols, namely, I-IV (Chart 1), on gold in order

* Abstract published in Advance ACS Abstracts, June 15, 1997.

(1) For a general review, see: (a) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: Boston, MA, 1991. (b) Ulman, A. *Chem. Rev.* 1996, 96, 1533-1554.

(2) Porter, M. D.; Bright, T. S.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* 1987, 109, 3559-3558.

(3) Fritzsche, H. D.; Avery, S.; Lynch, M.; Futsch, T. *Langmuir* 1987, 3, 408-418.

(4) Nuzzo, R. G.; Ziegler, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* 1987, 109, 763-770.

(5) Berr, C. D.; Trougham, E. S.; Tao, Y. T.; Brill, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1988, 110, 821-825.

(6) Leblond, P.; Whitesides, G. M.; Farhan, A. N.; Tao, Y. T.; Allara, D. L.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1991, 113, 7152-7157.

(7) Walczak, M. M.; Chung, C.; Stolz, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* 1991, 113, 2370-2378.

(8) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* 1991, 113, 3625-3637 and 3637-3638.

(9) (a) Strong, L.; Whitesides, G. M. *Langmuir* 1988, 4, 546-558. (b) Dubois, L. H.; Ziegler, B. R.; Nuzzo, R. G. *J. Chem. Phys.* 1989, 90, 678-682. (c) Porter, P.; Eisenberg, P.; Li, J.; Camillone, N.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Tao, Y. T.; Allara, D. L.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1991, 113, 7152-7157.

(10) Walczak, M. M.; Chung, C.; Stolz, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* 1991, 113, 2370-2378.

(11) Widge, C. A.; Alves, C. A.; Porter, M. D. *J. Am. Chem. Soc.* 1991, 113, 2806-2810.

(12) Alvim, G. A.; Smith, E. L.; Porter, M. D. *J. Am. Chem. Soc.* 1992, 114, 1222-1227.

(13) Sabatani, E.; Cohen-Bowik, J.; Strieding, M.; Rubinstein, I. *Langmuir* 1991, 7, 2874-2885.

(14) Tour, J. M.; Jones, L.; Ferguson, D. L.; Lembo, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parkin, A. N.; Attie, S. V. *J. Am. Chem. Soc.* 1995, 117, 8529-8534.

(15) Kwan, W. S. V.; Arakawa, L.; Miller, L. L. *Langmuir* 1991, 7, 1418-1428.

(16) Dpirani, A.; Zehner, R. W.; Huang, R. P.; Guyot-Stennett, P.; Sliu, L. R. *J. Am. Chem. Soc.* 1995, 117, 5316-5320.

(17) Lee, Y. J.; Jeon, T. C.; Park, W. K.; Kim, R. *Langmuir* 1995, 11, 5230-5237.

(18) Hunsicker, J. E.; Pardo-Schwarz, T. A.; Murray, R. W. *Langmuir* 1995, 11, 3277-3283.

(19) Evans, S. D.; Trankler, E.; Ulman, A.; Porter, N. J. *Am. Chem. Soc.* 1991, 113, 4121-4131.

(20) Tao, Y. T.; Chang, S. C.; Ma, L. F. *J. Chin. Chem. Soc.* 1995, 42, 659-668.

(21) Cheng, S.-C.; Chao, L.; Tao, Y.-T. *J. Am. Chem. Soc.* 1994, 116, 6792-6805.

(22) Wolf, H.; Ringsdorf, H.; Delamar, E.; Takami, T.; Kono, H.; Michel, B.; Garber, C.; Jochke, M.; Skir, H. J.; Bamberg, E. *J. Phys. Chem.* 1985, 89, 7102-7107.

(23) Crocker, S. E.; Strieter, C. M. *Langmuir* 1995, 11, 1252-1254.

(24) (a) Bryant, M. A.; Jon, S. L.; Pemberton, J. E. *Langmuir* 1992, 8, 752-756. (b) Wells, M.; Dermody, D. L.; Yang, H. C.; Kim, T.; Crooks, R. M.; Rizzo, A. J. *Langmuir* 1996, 12, 1862-1868.

(25) Delamar, E.; Michel, B. *Thin Solid Films* 1995, 273, 54-59.

(26) Wenz, A.; Drenthberger, C.; Wolf, H.; Wolf, J. J.; Buck, M. *Langmuir* 1996, 12, 5385-5387.

(27) Gavril, R. L.; Chadwick, J. E.; Severance, D. L.; McDonald, N. A.; Mies, D. C. *J. Am. Chem. Soc.* 1995, 117, 11563-11571.

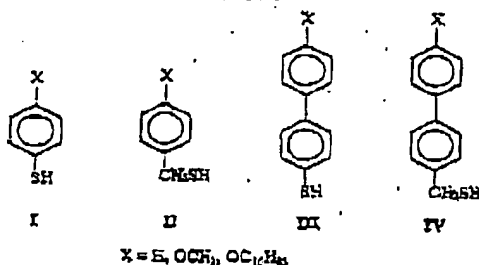
(28) Zhang, L.; Beck, T. L.; Young, J. T.; Bozko, F. J. *Langmuir* 1996, 12, 1227-1234.

S0743-7463(97)00098-X CCC: \$14.00

© 1997 American Chemical Society

Structure Evolution of Thiol Monolayers

Chart 1



to delineate factors that determine the structural order. Here the adsorbate-adsorbate interaction is manipulated in two ways. First, along the line of aforementioned packing promoted by intermolecular attractions, we systematically examine monolayer structures as a function of the number of rings involved and the length of the alkyl chain connected to the ring. Second, we perturb the steric conformation of head groups by inserting one methylene unit in between the aryl and the mercapto group (i.e., compounds II and IV). The results show, for the first time, that the insertion of the methylene unit can turn ill-defined thiophenol monolayers into well-ordered SAMs of benzyl mercaptans. In addition, depending on the length of a para-substituted alkoxy group, various structural order and packing density were obtained for thiophenol. A simulation model derived by Sellers *et al.*¹⁰ is adopted to elucidate the discrepancy arising from the insertion of the methylene unit. The different behavior is attributed to a counterbalance of intermolecular interaction and bond angle preference at the sulfur atom (sp³ versus sp).

Experimental Section

Materials. Thiophenol, anisyl mercaptan, and benzyl mercaptan were obtained from Aldrich and used directly. 4-Mercaptobiphenyl mercaptan, 4-biphenylmethanethiol, (4,4'-methoxybiphenylmethanethiol) and (4,4'-hexadecyloxybiphenyl)methanethiol were prepared by thioarene substitution of corresponding benzylic bromides followed by hydrolysis.²¹ The 4-biphenylthiol and 4,4'-methoxybiphenylthiol were synthesized from corresponding aryl bromide by metal-halogen exchange followed by sulfur quench. 4,4'-Hexadecyloxybiphenylthiol was prepared by sodium ethanethiolate substitution of the corresponding bromide followed by selective dealkylation of the resulting thioether.²⁴

Substrate Preparation. The gold substrates were prepared by vapor deposition of about 200 nm of gold (99.99% purity) onto freshly cleaved 1-in. mica sheets at a rate of 1 nm/s under a pressure of 9×10^{-7} Torr using an Ulvacryo-pumped evaporator. The vacuum chamber was back-filled with high-purity nitrogen after 45 min after deposition. The gold substrates were transferred to a furnace and annealed at 300 °C for 4 h. The roughness factor for substrates prepared under these condition was estimated to be 1.2.²⁵ The gold electrodes were cleaned in a UV ozone cleaner for 1 h and washed with ethanol right before these substrates were immersed in thiol solution. For IR measurement, 2-in. silicon wafers were used as the substrate in gold deposition. An adhesion layer of chromium (5–10 nm) was deposited before gold evaporation.

Monolayer Preparation. Thiols with one phenyl ring are dissolved in ethanol in a concentration of 1 mM. Compounds

(28) Tarkenton, L.; Tice, M.; Tice, M.; Chandra, D.; Montanari, M. *Synthesis* 1983, 751–755.

(29) Widny, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* 1991, 310, 333–349.

(30) Sellers, R.; Ullman, A.; Shindman, Y.; Edes, J. E. *J. Am. Chem. Soc.* 1993, 115, 8322–8340.

Langmuir, Vol. 15, No. 15, 1997 4019

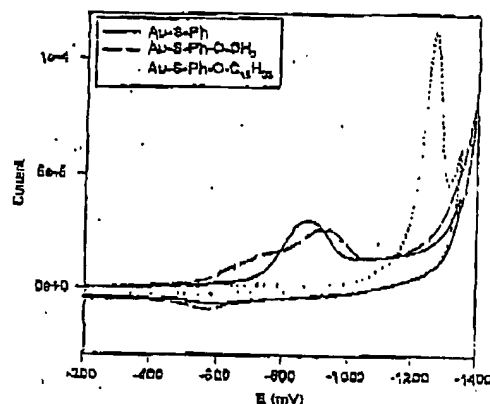


Figure 1. Cyclic voltammograms for Au-S-Ph, Au-S-Ph-O-CH₃, and Au-S-Ph-O-C₂H₅ monolayers.

containing two aromatic rings are less soluble and were first dissolved in a minimum amount of THF, and then ethanol was added to make up the final solution of 0.25 mM. Substrates were immersed in solution for at least 24 h. Samples were washed with THF and ethanol successively and dried with a flow of argon gas or spun-dried prior to use.

Electrochemical Measurement. A CV-27 potentiostat or a 100S electroanalysis system (Bioanalytical Systems, West Lafayette, IN) was used in cyclic voltammetry measurements. A conventional three-electrode cell was used with the area of the working electrode defined by the opening in an inert elastomer O-ring (0.68 cm²). A Pt coil auxiliary electrode and an Ag/AgCl/5 M NaCl reference electrode were used; all voltages were recorded with respect to this reference electrode. The supporting electrolyte was 0.5 M KOH (99.99% purity) in distilled, deionized water. The solution was purged with argon for 10 min prior to the experiment. The applied potential was cycled between -0.2 and -1.95 V at a scan rate of 100 mV/s with an initial potential of -0.2 V.

STM Measurements. STM measurements were carried out with a NanoScope II (Digital Instruments, Santa Barbara, CA) using a commercial Pt/Ir tip or a tungsten tip which was electrochemically etched in 1 M KOH. The images were calibrated by imaging Au(111) or HOPG (highly oriented pyrolytic graphite) in air.

Details of infrared measurements, ellipsometry measurements, and contact angle measurement were described previously.¹⁰

Results

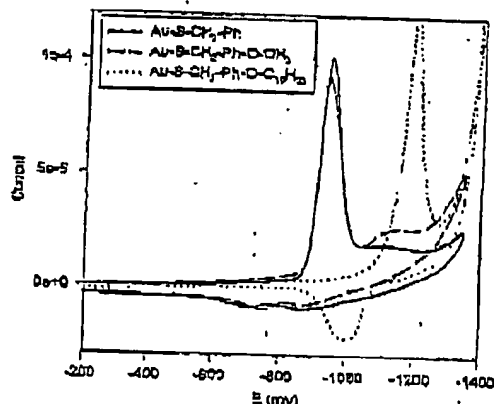
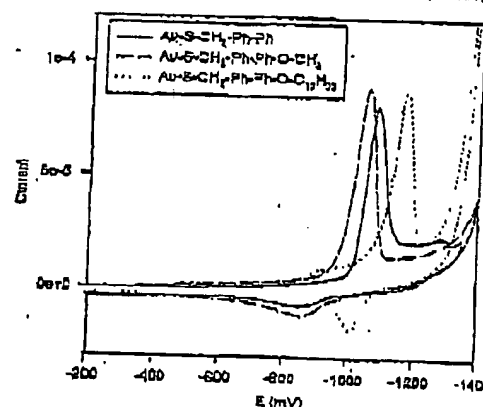
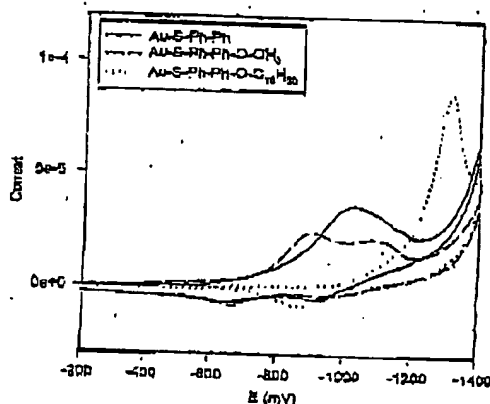
Electrochemical Measurement. The typical linear sweep voltammograms for the four series of monolayers on Au are shown in Figures 1–4. A summary of the desorption peak potentials and calculated surface coverages is shown in Table 1. In general, the peak on the reductive scan represents the desorption of the monolayer from the gold electrode. The area under the peak relates the number of molecules that were reductively desorbed from the surface as thiolate assuming a one-electron reduction process²⁶ and is directly related to the surface coverage. The peak potential has been shown to depend on the hydrocarbon chain length of the thiolate and such dependence is suggested to be related to the potential required to establish a potential gradient through the film that induces an ion flux sufficient to support the reduction process. It is noted that for the series II and IV, all the desorption peaks are rather sharp and well defined, whether it is unsubstituted or substituted with alkoxy group of different length. Moreover, the surface

4020 Langmuir, Vol. 13, No. 15, 1997

Tao et al.

Table 1. Packing Density ($\times 10^{-10}$ mol/cm²) and the Desorption Potential (mV) in Parentheses of Aromatic-Derived Thiols on Evaporated Au Using Electrochemically Reductive Desorption Method

| | I | II | III | IV |
|-------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| X = H | 4.4 \pm 0.4 (-848) | 5.1 \pm 0.3 (-921) | 5.1 \pm 0.7 (-926) | 8.0 \pm 0.3 (-1081) |
| X = OCH ₃ | 5.1 \pm 0.5 (-921) | 4.1 \pm 0.3 (-839) | 5.4 \pm 0.8 (-907) | 8.0 \pm 0.1 (-1037) |
| X = OC ₆ H ₁₃ | 6.6 \pm 0.6 (-1216) | 8.0 \pm 0.4 (-1152) | 7.7 \pm 0.3 (-1305) | 7.5 \pm 0.3 (-1157) |

Figure 2. Cyclic voltammograms for Au-S-CH₂-C₆H₅, Au-S-CH₂-C₆H₄-O-CH₃, and Au-S-CH₂-C₆H₄-O-C₁₀H₂₁ monolayers.Figure 4. Cyclic voltammograms for Au-S-CH₂-C₆H₅, Au-S-CH₂-C₆H₄-C₆H₄-C₆H₅, and Au-S-CH₂-C₆H₄-C₆H₄-C₆H₄-C₆H₅ monolayers.Figure 3. Cyclic voltammograms for Au-S-C₆H₅-C₆H₅, Au-S-C₆H₄-C₆H₄-O-CH₃, and Au-S-C₆H₄-C₆H₄-O-C₁₀H₂₁ monolayers.

coverages as calculated from the area under the peaks are similar irrespective of the substituent group on the aromatic ring. And the value is also close to that for the saturated *n*-hexadecanethiolate monolayer on gold, 7.8×10^{-10} mol/cm², equivalent to 21.5 Å²/molecule. For *n*-hexadecanethiolate monolayer, an overlayer of ($\sqrt{3} \times \sqrt{3}$)R30° was shown by various methods, and a packing density of 7.7×10^{-10} mol/cm² (21.6 Å²/molecule) is expected for such an overlayer.²⁰ Thus compounds in these two series most likely occupy a similar lattice as that of *n*-hexadecanethiolate monolayer. The desorption peak potential shows a trend to become more negative with increasing substituent chain length in the same series. The trend is more significant for the monophenyl system

(~240 mV difference in going from unsubstituted or methoxy-substituted to hexadecyloxy substituted) than the biphenyl system (~100 mV for the corresponding change). These are consistent with the increasing difficulty in the penetration of ions through the film during reduction.²¹ The shorter (monophenyl) system is more sensitive to the addition of shielding layer than the longer (biphenyl) system. The desorption peak potential is also more negative for the biphenyl series than the monophenyl series, with the same substituent group. The trend again is more significant for short chain (or unsubstituted) derivatives than the long chain derivatives.

On the other hand, for series I and III, the desorption peak shapes for the unsubstituted and methoxy-substituted ones are rather broad and ill-defined. More than one peak was also observed. Only with the C16-substituted ones, a sharper and well-defined curve was obtained. The packing density depends very much on the substituent group on the aromatic ring, ranging from 4.4×10^{-10} mol/cm² (37.8 Å²/molecule) for thiophenol to 8.6×10^{-10} mol/cm² (25.2 Å²/molecule) for hexadecyloxy-substituted thiophenol. With the biphenyl system, the packing density increases from 5.1×10^{-10} mol/cm² (32.6 Å²/molecule) for the unsubstituted one to 7.7×10^{-10} mol/cm² (21.6 Å²/molecule) for the hexadecyloxy-substituted one. Thus for monolayers of series I and III with X = H, the coverages are only about 60% of that of a full ($\sqrt{3} \times \sqrt{3}$)R30° monolayer, implying each molecule is occupying a larger coverage area than in the corresponding case of II and IV. With increasing chain length of the substituent, the packing becomes denser. It is further noted that the desorption peak potentials do not differ by much between series I and III for the same substituent group, except for the long chain substituted one. This is in opposite trend as that observed for series II and IV, which could imply that the aromatic groups did not pack well in the adsorbed state to block the flux of ions during the reduction.

Infrared Reflection Absorption Spectra. Reflection-absorption IR spectra of monolayers of the four series

Structure Evolution of Thiol Monolayers

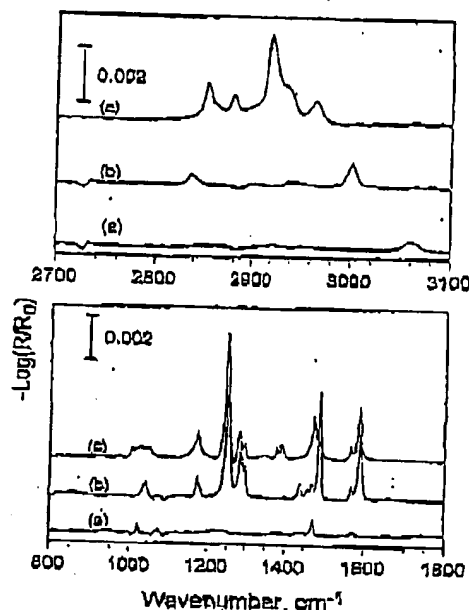


Figure 5. Infrared reflection absorption spectra for (a) Au-S-C₆H₅, (b) Au-S-C₆H₄-O-CH₃, and (c) Au-S-O-C₆H₄-O-C₆H₁₃ monolayers.

Table 2. Infrared Ring-Stratifying Frequency of Aromatic-Substituted Thiols on Evaporated Au and the Shift from Corresponding Value in KBr Sample, cm⁻¹

| | I | II | III | IV |
|-------------------------------------|----------|---------|----------|---------|
| X = H | 1472, -6 | 1494, 0 | 1475, -8 | 1488, 2 |
| X = OCH ₃ | 1488, -7 | 1518, 8 | 1479, -7 | 1501, 0 |
| X = OC ₆ H ₁₃ | 1488, -9 | 1514, 1 | 1475, 0 | 1501, 0 |

of compounds were taken. A representative series (for compound I) is shown in Figure 5. (The others are supplied as Supporting Information.) In general, the peak patterns in the C-H stretching region are very similar for the same substituent. Thus for C₁₆ substituted cases, the peak positions for methylene stretches (at 2918 and 2850 cm⁻¹) respectively for II and shifted less than 2 cm⁻¹ to higher end for the other three series) indicate close packing, if not a perfectly crystalline state of the chains. There are some variations in the relative intensities, which should be dependent on the exact chain tilt and twist. The methoxy-substituted ones all exhibit the same intensity for ν_s (OCH₃) at around 3062 cm⁻¹ and ν_s (OCH₃) around 2880 cm⁻¹. The only major feature for the unsubstituted ones is a weak band around 3082 cm⁻¹, which is assigned as the aromatic C-H stretch. In the low-frequency region, of particular interest is the peak positions for the ring stretch mode occurring at around 1472–1515 cm⁻¹ when compared to the KBr spectra of isotropic sample. The stretching frequency of the aromatic ring of monolayers I and III on Au shifted to lower values (by 6–9 wave-numbers) as compared to that in KBr spectra, except with X = C₁₆ for III, whereas for monolayers of II and IV there is no change or a slightly positive shift in this ring-stretching frequency as compared to that in the KBr spectra (Table 2). The implication of these trends will be discussed later.¹¹

Langmuir, Vol. 15, No. 15, 1997 4021

Table 3. Ellipsometric Thicknesses of Aromatic-Substituted Thiol Monolayers on Evaporated Au (Å)

| | I | II | III | IV |
|-------------------------------------|------|------|------|------|
| X = H | 1.3 | 2.4 | 9.4 | 10.3 |
| X = OCH ₃ | 1.8 | 5.2 | 10.4 | 13.9 |
| X = OC ₆ H ₁₃ | 22.3 | 28.2 | 50.6 | 33.3 |

Scanning Tunneling Microscopy Measurement. STM measurements show that the annealed bare gold substrates exhibit smooth plateaus with average size of ca. 50 nm in width. Images obtained on plateaus and terraces are composed of hexagonally close packed atoms with nearest-neighbor spacing of 0.25 ± 0.3 Å, indicative of Au(111) orientation. All four series of thiols significantly affect the substrates, resulting in morphological features of pits and jagged step edges which are characteristic of α -alkanethiol monolayers on gold.^{14,25} Because of the concerns of monolayer structures interfering with the STM tip due to the less conductive long alkyl chains, our report will concentrate on unsubstituted ones (X = H).

For monolayers of benzyl mercaptan (II), STM images always display a highly ordered hexagonal pattern. Figure 6a is a representative image obtained with 2 GΩ tunneling impedance (a bias voltage and tunneling current of 1.0 V and 0.5 nA, respectively). Under this condition, there is no indication of destructive imaging. Only one lattice structure is observed. The unit cell dimension is 4.9 ± 0.1 Å and the angle between lattice vectors is $55 \pm 5^\circ$, consistent with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. The dark defect shown in the image also exhibits the same lattice parameters which can be seen clearly by adjusting the image contrast. For monolayers of 4-biphenylmethanethiol (IV), the adlayer adopts preferentially a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, although an unassigned local structure is also found.²⁶ A typical image of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is presented in Figure 6b, which was obtained with 1 GΩ tunneling impedance. We notice that the imaging quality of series IV is, in general, not as decent as that of benzyl mercaptan (II). The origin of this difference is probably arising from the fact that the tunneling barrier of IV monolayers is an aryl ring thicker than those of II.

In contrast, for monolayers of series I and III with X = H and OCH₃, neither periodic pattern nor molecularly resolved images are observed, coherent with the finding of a previous STM study by Dhirani *et al.*¹⁶ In the case of (hexadecyloxy)phenylthiol (I with OC₆H₁₃), we observed a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer in only a few occasions. The domain size is as small as ca. 4 nm. The film structure appears predominantly disordered.

Ellipsometric Thickness Measurement. The ellipsometric thicknesses of these monolayers are collected in Table 3. Qualitatively, the benzyl mercaptan derivatives (II and IV) are thicker, when compared with thiophenol analogues (I and III), presumably because of the additional CH₂ unit in the benzyl mercaptan system. The biphenyl systems (III and IV) are also thicker when

(21) Smid, J.; Hirschman, D. R. *J. Phys. Chem.* 1957, 61, 3277–3178.

(22) (a) Kim, Y.-T.; Bard, A. J. *Langmuir* 1992, 8, 1090–1102. (b) McCarty, R. J.; Dunaway, D. J.; Willett, R. J. *Langmuir* 1993, 9, 2770–2774. (c) Pinner, C. E.; Taylor, M. J. *Langmuir* 1994, 10, 2254–2258. (d) Sandogha-Hachem, J. A. M.; Schenckberger, C.; Fekedule, L. G. *J. Phys. Chem.* 1994, 98, 6325–6334.

(23) We have observed a local structure exhibiting stripe modulation running across pits and line defects. The nearest-neighbor spacings along two primitive unit cell vectors are 4.0 ± 0.4 and 5.0 ± 0.5 Å and the angle between the vectors is $88 \pm 7^\circ$. Although the pattern looks like a rectangular $p \times \sqrt{3}$ structure, the area of the unit cell is too small to be the high-millimetry. At the present time, we are not able to assign a commensurate structure for this adlayer.

4022 Langmuir, Vol. 12, No. 15, 1997

Tao et al.

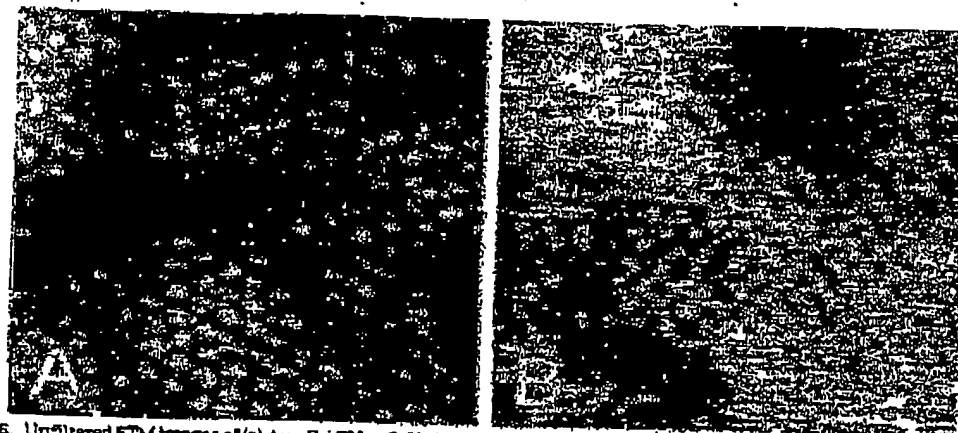


Figure 6. Unfiltered STM images of (a) Au-S-CH₂-C₆H₅ (image size 8 × 8 nm, $I_t = 0.3$ nA, $V_{bias} = 1.0$ V, nearest-neighbor spacing 4.9 ± 0.1 Å) (b) Au-S-CH₂-C₆H₄-C₆H₅ (image size 8 × 8 nm, $I_t = 0.5$ nA, $V_{bias} = 600$ mV, nearest-neighbor spacing 4.9 ± 0.3 Å).

Table 4. Contact Angle (deg) of H₂O on the Aromatic-Derivatized Thiol Monolayers on Evaporated Au

| | I | II | III | IV |
|--------------------------------------|-----|-----|-----|-----|
| X = H | 70 | 63 | 80 | 89 |
| X = OCH ₃ | 88 | 84 | 50 | 66 |
| X = OC ₁₂ H ₂₅ | 109 | 112 | 112 | 111 |

compared with monophenyl analogues (I and II), as one would expect for the additional phenyl group in the biphenyl system. However, in an absolute sense, the observed thicknesses for the unsubstituted or short-chain substituted ones are thinner than the expected values from the dimension of the molecules involved. Furthermore, the difference between each series is more than that expected for the group involved (1.4 Å for a CH₃ group and 7 Å for a phenyl group). These may be due to the uncertainty associated with ellipsometry measurement (index of refraction, surface contamination on "bare" gold \dots) as well as different packing density in each series, as evidenced by the electrochemical data. The ellipsometry data here can only serve as a qualitative support of the "monolayer" nature of the adsorbed film.

Contact Angle Measurement. Water contact angle values are reported in Table 4. It can be seen that the water contact angles on II and IV monolayers are higher than those on the analogues in I and III, but the difference decreases with increasing the length of X. While it can be argued that as the substituent chain length increases, the contact angle is less sensitive to the underlying substrate. It could also imply that the difference in the structure between I and II (or III and IV) diminishes as X increases in chain length.

Discussion

The data appear to fall into two categories. The first category includes benzyl mercaptans (II) and 4-biphenylmethanethiols (IV), both of which have a CH₂ unit between the thiol head group and the aromatic ring. They give well-defined cyclic voltammetry behavior in that the reductive wave is sharp and more uniform. The coverages correspond well to that of a close-packed *n*-alkanethiol monolayer. These adsorbates are expected to have a packing scheme similar to that of the *n*-alkanethiol, i.e., $\sqrt{3} \times \sqrt{3}$ R30° overlayer, as also evidenced by STM

measurements. The second category includes thiophenols and biphenylthiols. In contrast with benzyl mercaptans, both thiophenol and *p*-methoxythiophenol gave a rather broad desorption peak and low surface coverage, which implies a rather ill-defined film structure and lower packing density. This is in agreement with STM observations and literature reports^{12,11} that thiophenol forms poor monolayers.¹⁴

The discrepancy between these two categories shows the significance of the inserted methylene unit. For compounds containing the methylene unit, II and IV, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice structure suggests the herringbone packing of phenyl or biphenyl moieties. Considering the dimension of the phenyl ring,³¹ a herringbone packing will require the aromatic planes orienting nearly vertical to the gold surface.¹² This geometry was also suggested for adsorption of dibenzyl disulfide on silver³¹ where the phenyl ring is "sticking up". For compounds without the methylene unit, I and III, the negative shifts in the IR frequency of the ring stretch mode region (from 1472 to 1515 cm⁻¹) are similar to that observed in the adsorption of diphenyl disulfide on silver,³¹ where a "lying-flat" geometry was proposed based on Raman spectroscopy. This negative shift suggests that the long axis of the benzene ring (the one passing through X and S) for compounds I and III is inclined toward the gold surface. This tilt creates steric hindrance which would occupy a larger space and diminish intermolecular attractions between neighboring phenyl rings, and thus results in a poorly defined monolayer. Given the resemblance of these compounds, the methylene unit is an intriguing factor in orienting the phenyl ring vertical to the surface.

The critical role of the methylene unit can be illustrated by an S-Ar binding scheme modeled by the quantum calculations of Sellers et al.³⁰ who proposed sp and sp³ hybridization with surface-S-C bond angles of 180° and 104°, respectively. In the case of saturated *n*-alkanethiol on Au(111), the trend in the odd-even effect observed in

(34) It is noted that a different conclusion was obtained for biphenylthiol from electron transfer rate measurement.¹² However, it is also noted in the same work that surface coverage measurements by ac impedance and gold oxide removal on a monolayer-covered surface indicated that biphenylthiol behaved more like thiophenol than *n*-phenylthiol in the monolayer assembly.

(35) van der Waals dimensions of a vertically oriented phenyl ring are 5.4 Å (width) × 3.5 Å (thickness).

Structure Evolution of Thiol Monolayers

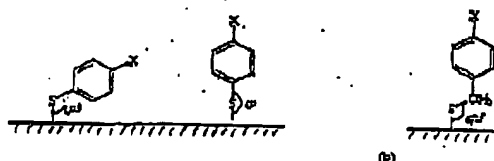


Figure 7. Possible orientation of monolayers of (a) thiophenol and (b) benzyl mercaptan derivatives on gold.

IR,^{6,7,10} which reflecting the orientation of the terminal methyl group, clearly implies a preference of sp^3 hybridization in the sulfur atom (or a bent Au-S-C bond angle) and a trans zigzag extension of the alkyl chain. A linear Au-S-C bond angle (or sp hybridization) has been invoked to rationalize a reversed trend in the odd-even effect observed on Ag.¹⁰ In the case of compounds I and III with X = H and OCH₃, the tilt orientation of phenyl ring implies that sp^3 hybridization is more favorable than sp hybridization (Figure 7a). For compounds II and IV, in order to adopt the close-packed $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, a bond angle of C-S-Au is required. Consequently, sp^3 hybridization appears to be the favorable one for compounds II and IV as well (Figure 7 b). In either category, the S atom adopts sp^3 hybridization when X = H or OCH₃. Therefore, the insertion of a methylene unit can relax the rigidity of the thiol head group and lead to a stronger intermolecular interaction.

For compounds I and III with a long chain substituent, such as a hexadecyl group, the electrochemical behavior is approaching that of the benzyl mercaptans. The same IR pattern in the CH stretching region also implies similar packing and orientation in the long alkyl chain portion. This would compel the long ends of the benzene ring to point nearly perpendicular to the surface. This is achieved by a greater surface-S-C bond angle or, equivalently, the adoption of sp hybridization at the sulfur atom, with energy compensated by a greater interchain interaction.

Langmuir, Vol. 13, No. 15, 1997, 4023

Conclusions

It is shown in this study that for phenyl-substituted thiols, the structure of a monolayer formed on gold is dependent on the location of the aromatic ring. With a methylene unit inserted between the phenyl ring and the thiol head group, a closely packed and ordered monolayer of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure can be formed. The substituent at the para-position increases the interchain interaction but does not change grossly the packing density and/or arrangement. With a thiol group directly attached to the aromatic ring, the para-substituent affects the packing in the monolayer. In the absence of a substituent or in the presence of a short chain, a less densely packed monolayer with coverage as low as 60% of that of a fully packed monolayer can result. A longer chain introduces greater interchain interaction and results in a higher coverage. The difference between these two categories of thiols is suggested to be a balance of the interchain interaction and the bonding geometry adopted at the thiolate head group. An sp^3 hybridization is suggested to be the favored state at the sulfur atom. This geometry allows the benzyl-type thiols to arrange the aromatic rings into a well-ordered packing but prohibit the thiophenol-type molecules to arrange their aromatic moiety. With a longer substituent at the para-position, greater packing interaction causes a change of bond angle (or a change of hybridization) to allow a tighter packing of the rings.

Acknowledgment Financial support from National Science Council, Republic of China, is gratefully acknowledged. C.H.C. gratefully acknowledges the Chemistry Department of National Sun Yat-sen University for a generous starting fund.

Supporting Information Available: Figures of infrared refraction absorbance spectra for II-IV monolayers (2 pages). Ordering information is given on any current masthead page.

LA9700984



**United States
Patent and
Trademark Office**

RECEIVED
CENTRAL FAX CENTER
AUG 03 2005

Return to:
USPTO
Home
Page
Finance
Online
Scheduling
Page

Deposit Account Statement

Requested Statement Month: July 2005
Deposit Account Number: 082395
Name: HITT GAINES, PC.
Attention:
Address: PO BOX 832570
City: RICHARDSON
State: TX
Zip: 75083
Country: UNITED STATES OF AMERICA

| DATE | SEQ | POSTING REF TXT | ATTORNEY DOCKET NBR | FEE CODE | AMT | BAL |
|---------|-----|--------------------|---------------------------|-------------|-------------|------------|
| 07/08 | 314 | 60696583 | SEYC-0001PV | 2005 | \$100.00 | \$3,424.00 |
| 07/11 | 126 | 10379147 | REITH | 1401 | \$500.00 | \$2,924.00 |
| 07/11 | 292 | 11143803 | A. LANDSCHAFT 7-7-7 | 8007 | \$20.00 | \$2,904.00 |
| ✓ 07/12 | 77 | 10727709 | | 1801 | \$790.00 | \$2,114.00 |
| 07/12 | 265 | 0139250572 | FSC-0014PH | 8014 | \$25.00 | \$2,089.00 |
| 07/13 | 41 | E-REPLENISHMENT | | 9203 | -\$2,500.00 | \$4,589.00 |
| 07/13 | 116 | 10323370 | ERBEN 3-48-3 | 1808 | \$180.00 | \$4,409.00 |
| 07/14 | 17 | 10875015 | D. GILL 15-36 | 8007 | \$20.00 | \$4,389.00 |
| 07/14 | 313 | 11178944 | A.LANDSCHAFT 9-1 | 1011 | \$300.00 | \$4,089.00 |
| 07/14 | 314 | 11178944 | A.LANDSCHAFT 9-1 | 1111 | \$500.00 | \$3,589.00 |
| 07/14 | 315 | 11178944 | A.LANDSCHAFT 9-1 | 1311 | \$200.00 | \$3,389.00 |
| 07/14 | 316 | 11178944 | A.LANDSCHAFT 9-1 | 1202 | \$250.00 | \$3,139.00 |
| 07/19 | 177 | 10405398 | 10/405398 | 1801 | \$790.00 | \$2,349.00 |
| 07/21 | 287 | 09626943 | KIZILYALLI 50-23 | 1402 | \$500.00 | \$1,849.00 |
| ✓ 07/22 | 1 | 10727709 | | 1801 | \$790.00 | \$1,059.00 |
| 07/25 | 3 | 10082776 | BENNETT 6-5 | 1801 | \$790.00 | \$269.00 |
| 07/25 | 4 | E-REPLENISHMENT | | 9203 | -\$2,500.00 | \$2,769.00 |
| 07/26 | 58 | 09993114 | 01-633 | 1251 | \$120.00 | \$2,649.00 |
| 07/27 | 48 | 09234351 | M.WILLIAMS 2 | 8007 | \$20.00 | \$2,629.00 |
| 07/27 | 61 | 10041148 | C.BERTHOUD22 | 1401 | \$500.00 | \$2,129.00 |
| 07/28 | 6 | E-REPLENISHMENT | | 9203 | -\$2,500.00 | \$4,629.00 |
| 07/28 | 13 | 10119475 | L.N.YAGATI 2 | 1801 | \$790.00 | \$3,839.00 |
| 07/29 | 5 | 09953581 | BRNS-0007 | 2201 | \$100.00 | \$3,739.00 |
| 07/29 | 6 | 09953581 | BRNS-0007 | 2202 | \$150.00 | \$3,589.00 |
| 07/29 | 222 | 08656629 | AVYA-04JP | 8007 | \$20.00 | \$3,569.00 |

START SUM OF SUM OF END

Attachment B

AUG. 3. 2005 6:01PM HITT GAINES 9724808865
Deposit Account Statement

NO. 1639 P. 17
Page 2 of 2

| BALANCE | CHARGES | REPLENISH BALANCE |
|------------|------------|-----------------------|
| \$3,524.00 | \$7,455.00 | \$7,500.00 \$3,569.00 |

[Need Help?](#) | [USPTO Home Page](#) | [Finance Online Shopping Page](#)

AUG. 3. 2005 5:56PM HITT GAINES 9724808865

PATENT & TRADEMARK
OFFICE

NO. 1639 P. 1

2005 AUG - 3 PM 3: HITT GAINES, P.C.
Intellectual Property Law & Related Matters
US PATENT & TRADEMARK
OFFICE

RECEIVED
CENTRAL FAX CENTER

AUG 03 2005

FACSIMILE TRANSMISSION

TO: USPTO
Examiner Waising Louie; Art Unit 2814

FAX NO. (571) 273-8300

FROM: Ronald J. Corbett

RE: Serial No.: 10/727,709
Attorney Docket No.: BAO 39
LUCT-125888

DATE: June 30, 2005

PAGES: 17 (including cover page)

If you do not receive the indicated number of pages, please notify the sender at the telephone number shown below. Thank you.

THE INFORMATION CONTAINED IN THIS FACSIMILE TRANSMISSION IS AN ATTORNEY-CLIENT PRIVILEGED, CONFIDENTIAL COMMUNICATION INTENDED FOR THE EXCLUSIVE USE OF THE INTENDED RECIPIENT NAMED ABOVE. IF YOU ARE NOT THE INTENDED RECIPIENT, OR ARE AN EMPLOYEE OR AGENT RESPONSIBLE FOR DELIVERING THIS TRANSMISSION TO THE INTENDED RECIPIENT, YOU ARE HEREBY NOTIFIED THAT ANY DISSEMINATION, DISTRIBUTION OR COPYING OF THIS TRANSMISSION IS STRICTLY PROHIBITED. IF YOU HAVE RECEIVED THIS TRANSMISSION IN ERROR, PLEASE NOTIFY THE SENDER IMMEDIATELY AT THE TELEPHONE NUMBER SHOWN BELOW AND MAIL THE ORIGINAL TRANSMISSION TO THE ADDRESS BELOW. WE WILL REIMBURSE YOU FOR ANY REASONABLE EXPENSE YOU MAY INCUR DOING SO. THANK YOU.

MESSAGE:

Please send fax confirmation to: 972-480-8865

Mailing Address: P.O. Box 832570, Richardson, Texas 75083-2570
Street Address: Palisades Central II, 2435 North Central Expressway, Suite 1300, Richardson, Texas 75080-2753 U.S.A.
Tel: (972) 480-8800 Fax: (972) 480-8865 firm@hittgaines.com

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.